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(21) International Application Number: PCT/EP96/04781 (22) International Filing Date: 31 October 1996 (31.10.96) (30) Priority Data: 1001553 2 November 1995 (02.11.95) NL (71) Applicant (for all designated States except US): AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): MAS CABRÉ, Francisco, René [NL/NL]; Max Havelaarstraat 30, NL-1183 NE Amstelveen (NL). PANNEKEET, Wilhelmus [NL/NL]; Jelgersmastraat 11, NL-2023 EM Haarlem (NL). SMAKMAN, Robert [NL/NL]; Raadhuisstraat 1, NL-1393 NW Nigtevech (NL). (74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Patent Dept. (Dept. APTA), P.O. Box 9300, NL-6800 SB Arnhem (NL).		(81) Designated States: CA, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: PROCESS FOR SYNTHESISING POROUS INORGANIC MATERIALS (57) Abstract <p>The invention pertains to a process for synthesising a porous inorganic material having an MoPD of 0.8-2.0 nm, characterised in that the synthesis is performed in the presence of templates containing one or more amphipolar compounds having at least two cationic or anionic head groups and a hydrophobic part. Preferably, at least a portion of the head groups of the amphipolar compound has a cationic nature. The process according to the invention makes it possible to synthesise novel porous mixed oxides, in particular metallocates, more in particular aluminosilicates, with an MoPD of 0.8-2.0 nm. These materials are especially attractive for use in catalysis.</p>		

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PROCESS FOR SYNTHESISING POROUS INORGANIC MATERIALS

- 5 The invention pertains to a process for synthesising porous inorganic materials in the presence of an amphipolar compound.

Porous inorganic materials, such as porous amorphous aluminas, silicas, silica-aluminas, and crystalline molecular sieves, are applied, int. al., in catalysis.

- 10 The catalytic activity and selectivity of porous inorganic materials, including molecular sieves, is dependent, int. al., on their pore size, since this determines the material's accessibility and sorption properties for molecules of a particular size. For that reason it has been attempted for many years to obtain porous inorganic materials, notably crystalline molecular sieves, having differing pore diameters. For instance, there are
- 15 the so-called "large pore molecular sieves," which have a pore diameter of the order of 0.7-1.2 nm, the best-known exponent of which is Y zeolite having a pore diameter of 0.8 nm. Other "large pore molecular sieves" include X zeolite, ALPO-5, ALPO-8, beta zeolite, MCM-22, MCM-36, and VPI-5. This last compound is an aluminium phosphate or a silicoaluminium phosphate with a pore diameter of 1.2 nm.

- 20 A novel development in this field is disclosed in WO 91/11390 in the name of Mobil. This patent application describes ultra-large pore materials, e.g., having a pore diameter determined by argon physisorption of the order of 2 nm and higher. Although the general description mentions a minimum pore diameter of 1.3 nm, the exemplified
- 25 compound with the smallest pore diameter is a silicate with a pore diameter of 1.5 nm. The examples provided in this publication mostly have to do with the preparation of a molecular sieve having a pore diameter of 4.0 nm, which is referred to as MCM-41.

- It has been found that, on the one hand, the known "large pore molecular sieves" do
- 30 not always have a sufficiently large pore diameter to admit the desired reactants, e.g., large hydrocarbon molecules, yet, on the other, the pore diameter of the MCM-41-type materials is too large to ensure sufficient catalytic activity. In consequence, there is need for molecular sieves having a diameter which lies between the diameters of the known "large pore" zeolites and the MCM-41-type materials. More in particular, there

is need for porous inorganic materials, in particular molecular sieves, which have a mode pore diameter of 0.8-2.0 nm.

5 In molecular sieve synthesis use is frequently made of templates. For instance, ZSM-5 and beta zeolite are synthesised in the presence of quaternary ammonium ions of the formula $R_1R_2R_3R_4N^+$, wherein R_1 , R_2 , R_3 , and R_4 are alkyl groups having fewer than 6 carbon atoms.

By contrast, the synthesis of ultra-large pore molecular sieves described in WO 91/11390 is carried out in the presence of micelle-forming template compounds
10 of the formula $R_1R_2R_3R_4Q^+$, wherein Q is a nitrogen atom or phosphorus atom and at least one of R_1 , R_2 , R_3 , and R_4 is an aryl group or alkyl group having 6-36 carbon atoms, and each of the other groups is selected from hydrogen and an alkyl group having 1-5 carbon atoms. The most frequently employed template compound in this publication is a cetyl trimethyl ammonium salt, e.g., a halide or hydroxide. The key
15 aspect of the use of these molecules is that in water above a certain concentration, the critical micelle concentration or CMC, they aggregate to form micelles, and it is these micelles which actually act as templates in the synthesis of the molecular sieves.

20 When synthesising molecular sieves, it is generally the case that the pore diameter of the obtained product is dependent on the size of the template employed. Accordingly, by varying the size of the template, it is possible in principle to vary the pore diameter of the obtained product. In actual practice, however, this process is subject to restrictions. For instance, when the object is to obtain products having a pore
25 diameter which lies between the beta zeolite and the MCM-41 pore diameter, two options present themselves.

On the one hand, an attempt can be made to increase the size of the quaternary ammonium ion used as the template in, say, the synthesis of beta zeolite by enlarging the alkyl groups present therein. However, this route is unsuccessful, since the
30 resulting molecules are either so poorly soluble under synthesis conditions that they are incapable of acting as a template compound, or they form micelles having a too

large cross-section to enable them to act as templates in the synthesis of products having a pore diameter in the desired range.

On the other hand, an attempt can be made to reduce the cross-section of the micelles used in the synthesis of MCM-41-type materials by shortening the quaternary ammonium ion chain tail length. However, this route is not successful either, since the
5 resulting molecules have such a high CMC that they will no longer form micelles under the molecular sieve synthesis conditions.

Very recently, experiments were carried out with templates which deviate from the
10 conventional quaternary ammonium structure.

Qisheng Huo et al. (Science, Vol. 268, pp. 1324-1327, 1995) describes the synthesis of mesoporous silicas in the presence of compounds of the formula $C_nH_{2n+1}N^+(CH_3)_2^-(CH_2)_5-N^+(CH_3)_2C_mH_{2m+1}$. These types of compounds, which have two hydrophilic head groups and hydrophobic tails, may be indicated as gemini compounds. The products
15 obtained in this reference all have a pore diameter above 2.0 nm.

S.A. Bragshaw et al. (Science, Vol. 269, pp. 1242-1244, 1995) describes the synthesis of mesoporous silicas and aluminas in the presence of polyethylene oxide compounds. The materials synthesised all have HK pore diameters of above 2.0 nm.

P.T. Tanev and T.J. Pinnavaia (Science, Vol. 267, pp. 865-687, 1995) describe the
20 synthesis of mesoporous silicas in the presence of neutral primary amines. The lowest pore diameter obtained is 1.6 nm. However, it has appeared from experiments that the synthesis of inorganic oxides with an MoPD of below 2.0 nm in the presence of neutral templates leads to products with less pore volume and surface area than synthesis in the presence of either cationic or anionic templates.

25

Therefore, there is need for a process for synthesising porous inorganic materials which have a mode pore diameter between 0.8 and 2.0 nm, using a template which is either cationic or anionic. The present invention provides such a process.

The process according to the invention is characterised in that a porous inorganic
30 material having an MoPD of 0.8 -2.0 nm, preferably 1.0-2.0 nm, more preferably 1.0-1.8 nm, is synthesised in the presence of templates containing one or more

amphipolar compounds having at least two cationic or anionic head groups and a hydrophobic part. Preferably, at least a portion of the head groups of the amphipolar compound has a cationic nature.

5 The use of amphipolar compounds having at least two cationic or anionic head groups and a hydrophobic part opens up a wide range of options. For instance, one may use an amphipolar compound having at least two cationic or anionic head groups and at least two hydrophobic tail groups.

10 With the length of the hydrophobic tail groups remaining the same, these compounds have a lower CMC than the corresponding single amphipolar compounds, which have one head group and one tail group. These compounds therefore form micelles at a tail length which is too short for the single amphipolar compounds to form micelles. This means that micelles can be obtained which have a smaller cross-section than that of the micelles which can be obtained with single amphipolar compounds. By using
15 these micelles as templates in the synthesis of porous inorganic materials, products can be obtained which have a diameter between 0.8 and 2.0 nm.

Suitable micelle-forming amphipolar compounds having at least two cationic head groups and at least two hydrophobic tail groups include the ions of formula (1)

20



wherein

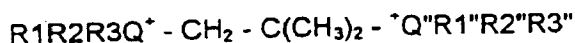
25 Q, Q', and Q'' may be the same or different and represent a nitrogen atom or phosphorus atom,

n and m each independently have a value of 1-8,

y has a value of 0-1000,

30 R₁, R₁', and R₁'' are independently selected from optionally substituted alkyl groups having 3-12 carbon atoms and optionally substituted aryl groups having 4-12 carbon atoms, R₂, R₂', R₂'', R₃, R₃', and R₃'' are each independently selected from hydrogen and optionally substituted alkyl groups having 1-6 carbon atoms, with the

proviso that each of R1, R1', and R1" contains more carbon atoms than each of R2 and R3, R2', and R2" and R3", respectively, R4, R4', R5, and R5' may be the same or different and are selected from hydrogen and optionally substituted methyl and ethyl. It should be noted that if n, m, and/or y has a value higher than 1, the additional groups formed as a result, Q", R4, R5, R4', R5', R1', and R2' need not necessarily have the same value as the other groups thus designated. For instance, the compound below, wherein n is 2, is also covered by formula (1).



10

Preferred compounds according to formula (1) for use in the process according to the invention are those wherein R4, R4', R5, and R5' all are hydrogen or methyl. Further preference is given to n and m having a value of 2-4. y preferably is 0-10, more preferably 0-4. R1, R1', and R1" preferably have 4-10 carbon atoms, most preferably 6-10. Preferably, all of R1, R1', and R1" are the same. R2, R2', R2'', R3, R3', and R3" are preferably all selected independently from methyl, ethyl, and propyl.

15

Examples of suitable micelle-forming amphipolar compounds according to formula (1) are:

- (2) $(CH_3)_2C_6H_{13}N^+ - CH_2 - CH_2 - {}^+NC_6H_{13}(CH_3)_2$
- (3) $(CH_3)_2C_6H_{13}N^+ - CH_2 - CH_2 - CH_2 - {}^+NC_6H_{13}(CH_3)_2$
- (4) $(CH_3)_2C_6H_{13}N^+ - CH_2 - C(CH_3)_2 - CH_2 - {}^+NC_6H_{13}(CH_3)_2$

20

These ions are neutralised by the presence of an equivalent amount of negative ions, e.g., halogen ions, nitrate ions, sulphate ions, or OH-ions. Halogen ions are generally preferred.

25

Other template compounds having at least two cationic head groups and at least two hydrophobic tail groups may also be employed. For instance, the amphipolar units can also be connected one to the other via the hydrophobic tails.

30

If the above compounds are used in the process according to the invention, the micelles containing the amphipolar compounds act as templates. In that case it is

essential that these micelles are formed under synthesis conditions. In this connection it should be noted that templates which contain an amphipolar compound with at least two cationic or anionic head groups and at least two hydrophobic tail groups can, if so desired, contain other components in addition to this amphipolar compound, e.g.,
5 other amphipolar compounds.

The templates containing one or more amphipolar compounds having at least two cationic or anionic head groups and a hydrophobic part to be used in the process of the present invention may also be made up of polymers which comprise at least two
10 cationic or anionic head groups and a hydrophobic part. In this case, the polymer molecules themselves generally function as template, without aggregating to form micelles. Examples of polymers suitable for use as template are poly-4-vinyl pyridinium derivatives such as poly-4-vinyl-1-methyl pyridinium halogenides, cationic polystyrene derivatives or poly(meth)acrylamide derivatives.

15 The process according to the invention can be employed to synthesise porous inorganic materials essentially made up of oxides of a single atom type, but equally to synthesise porous inorganic materials containing oxides of several types of atoms. For instance, the process according to the invention can be used to synthesise porous
20 aluminas or silicas, but equally to synthesise porous metallosilicates, such as aluminosilicates, titanium silicates, zirconium silicates, etc.

More in particular, the present invention has made it possible for the first time to synthesise porous mixed metal oxides with an MoPD of 0.8-2.0 nm. These mixed metal oxides, which contain at least 0.2 wt.% of a first oxide and a total of further
25 oxides of at most 99.8 wt.% are also part of the present invention. Preferably, the novel porous mixed oxide is a porous metallosilicate. Aluminosilicates are particularly preferred.

Generally speaking, the novel compounds which can be synthesised using the
30 process according to the invention are of the following formula:



wherein

X is a trivalent element such as aluminium, iron or gallium,

Y is a tetravalent element such as silicon or germanium,

Z is a pentavalent element such as phosphorus,

5 O represents an oxygen atom,

N is a counterion such as sodium,

and R is the amphipolar compound,

with a, b, c, d, e, and r standing for the molar fractions of the different components,
and the compound as a whole being neutral.

10 As indicated above, the process according to the invention is pre-eminently suited to
be used for synthesising compounds of the aforesaid formula wherein X is aluminium,
Y is silicon, and c has the value 0.

The compound according to the formula above is such as it is obtained fresh from the
synthesis reaction. Generally, this material will be subjected to some treatment, say,
15 an extraction step and/or a calcination step, to remove the amphipolar compound R
from the composition. The counterion N in this freshly obtained product frequently is
sodium, which is there as a result of its presence in the synthesis mixture. In general,
this sodium will be replaced with other counterions, such as H^+ , NH_4^+ , etc. Procedures
for removing the amphipolar compound via calcination and counterion exchange
20 processes are well-known to the skilled person and have, for example, been
described for MCM-41, int. al., in WO 91/11390.

The process according to the invention can be performed as follows.

In a first step, a solution of the amphipolar compound is prepared in a solvent. The
25 solvent as a rule is water. If the template contains more than one amphipolar
compound, that is, if it is micelles of the amphipolar compound which act as template
rather than the amphipolar compound itself, the concentration of the amphipolar
compound in the solvent has to be selected such as will give a concentration of the
amphipolar compound in the reaction mixture under reaction conditions which is
30 higher than this compound's CMC, so that the reaction mixture will contain micelles.

Generally, the concentration of the amphipolar compound in the reaction medium will be between 1 and 20 wt.%, calculated on the water phase.

Next, the sources of the oxides to be incorporated into the composition have to be added to the solution of the amphipolar compound. Should the occasion arise, other components such as an alkali source can be added to the resulting mixture.

The resulting mixture is subsequently crystallised at a temperature in the range of 0° to 250°C, preferably 10-175°C, more preferably 10-100°C. If carried out at a temperature above 100°C, the reaction should be performed under pressure to ensure that it takes place in the liquid phase. Carrying out the reaction under autogenous pressure is appropriate. The pH of the mixture has a value in the range of 3 to 14, preferably 9-14.

Suitable silica sources include precipitated amorphous silica, amorphous silica prepared by flame hydrolysis, water glass, organic silicates, and crystalline inorganic silicates such as zeolites or clays. Suitable alumina sources include alumina, aluminium oxyhydroxide, aluminium hydroxide, sodium aluminate, aluminium sulphate, aluminium nitrate, aluminium chlorohydrate, and organic aluminium compounds such as aluminium alkoxides. Suitable alkali sources include the oxides or hydroxides of the Group IA and Group IIA elements, or compounds of these elements and silica or alumina, such as water glass or sodium aluminate, or quaternary ammonium bases or guanidine bases. Following crystallisation the material is isolated, washed with water, dried, and, optionally, calcined at a temperature in the range of 400° to 750°C in an air and/or nitrogen atmosphere.

Products prepared by the process according to the invention, and in particular the new mixed metallosilicates with an MoPD of 0.8-2.0 nm, can be used in a wide range of applications. They are especially suitable for use in catalysis, for example, cracking or hydrocracking of hydrocarbon feeds, isomerisation, alkylation, etc.

Example 1

To 106.63 g of demineralised water in a 250 ml PTFE (polytetrafluoroethylene) reaction vessel were added successively, with stirring:

- 1.61 g of 99.7 wt. % NaOH,

- 9.18 g of 98 wt. % amphipolar compound

$[\text{C}_6\text{H}_{13}(\text{CH}_3)_2\text{N}^+ - \text{CH}_2 - \text{CH}_2 - \text{N}^+(\text{CH}_3)_2\text{C}_6\text{H}_{13}]\text{Br}_2$,

- 11.30 g of amorphous silica KETJENSIL SM 830, 92.8 wt. % SiO_2 , 0.33 wt. % Al_2O_3

The $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{H}_2\text{O}$ molar ratio in the reaction mixture was 1: 0.002: 34.20.

The mixture was homogenised by stirring for one hour at room temperature. Next, the resulting homogeneous mixture was reacted, with stirring, for 24 hours at a temperature of 95°C, after which the product was filtered off, washed with water, and dried at room temperature.

To determine the characteristics of the product, a small portion was calcined at 540°C and the nitrogen adsorption curve of the calcined product determined. The data obtained in this manner is listed below.

The process specified above was repeated with the amounts of caustic soda and amphipolar compound, the reaction temperature, and the reaction time being varied. The outcome of these experiments is listed below.

No	Molar ratio		Reaction		SPESA	PV<10nm	MoPD	PV \pm 0.1MoPd	
			time	temp					
	QUAT	NaOH	Hr	°C	m ² /g	ml/g	nm	%	ml/g
1A	0.115	0.230	24	95	592	0.298	1.52	31	0.092
1B	0.115	0.345	24	95	388	0.200	1.38	26	0.053
1C	0.058	0.115	24	95	224	0.087	1.52	21	0.019
1D	0.115	0.230	91	33	322	0.120	1.27	18	0.022
1E	0.115	0.230	15	115	101	0.053	1.52	12	0.007
1F	0.058	0.230	24	95	497	0.246	1.52	28	0.068

In the above table QUAT indicates the amount of amphipolar compound added to the reaction mixture.

- 5 The specific surface area and the pore size distribution of the specimens were obtained from the nitrogen adsorption isotherm determined at 78 K.

The SPESA (single point equivalent surface area) is calculated from the adsorption V_a at a pressure ratio P/P_0 of 0.30 according to the formula:

$$\text{SPESA (m}^2/\text{g)} = 4.353 (1 - P/P_0) V_a \text{ (ml/g at standard T and P)}$$

- 10 V_a is interpolated from adjacent points in the adsorption isotherm.

The pore size distribution was determined according to the method Broekhoff-De Boer (J. Catal. 9, 8-14 (1967)). Because the pore size distribution of these types of products is relatively steep, adjustment of the calculation method was necessary. A

15 matrix was made with 70 steps of 0.05-0.2 nm in the diameter range of 1.25-10 nm and 28 steps of 1-20 nm in the diameter range of 10-200 nm. To determine the values for P/P_0 in accordance with the modified Kelvin equation for the model of cylindrical pores which are open at both sides, such as used in the method Broekhoff-De Boer, the amount of adsorbed liquid nitrogen is interpolated from the adsorption isotherm.

- 20 From this data cumulative and differential pore size distributions are calculated. This leads to the pore volume in pores with a diameter below 10 nm, the mode pore diameter (MoPD), which is defined as the diameter corresponding to the maximum in

the differential curve peak of the pore volume plotted against the pore diameter, and the pore volume present in pores with a diameter 10% below and above the MoPD. The remaining designations in the above table are self-explanatory.

5 Example 2

To 104.51 g of demineralised water in a 250 ml PTFE reaction vessel were added successively, with stirring:

- 1.61 g of 99.7 wt.% NaOH,
- 10 - 9.18 g of 98 wt.% amphipolar compound
 $[\text{C}_6\text{H}_{13}(\text{CH}_3)_2\text{N}^+ - \text{CH}_2 - \text{CH}_2 - \text{N}^+(\text{CH}_3)_2\text{C}_6\text{H}_{13}]\text{Br}_2$,
- 2.77 g of aluminium chlorohydrate, 23.3 wt.% Al_2O_3 ,
- 11.30 g of amorphous silica KETJENSIL SM 830, 92.8 wt.% SiO_2 , 0.33 wt.% Al_2O_3 .

- 15 The mixture was homogenised by stirring for one hour at room temperature. Next, the resulting homogeneous mixture was reacted, with stirring, for 24 hours at a temperature of 95°C, after which the product was filtered off, washed with water, and dried at room temperature.

- To determine the product's characteristics, a small portion was calcined at 540°C and
 20 the nitrogen adsorption curve of the calcined product determined. The data obtained in this manner is listed below.

No	Molar ratio mol H ₂ O = 34.20				SPESA	PV<10nm	MoPD	PV ± 0.1MoPd	
	QUAT	NaOH	Al ₂ O ₃	SiO ₂	m ² /g	ml/g	nm	%	ml/g
2A	0.115	0.230	0.038	1.00	437	0.221	1.33	18	0.039
2B	0.115	0.230	0.038	1.00	430	0.215	1.38	22	0.047
2C	0.058	0.230	0.038	1.00	425	0.230	1.27	14	0.031

- To get an indication of the catalytic cracking activity of a product it can be subjected to
 25 the Alpha test to obtain an Alpha value. The Alpha value is an approximate indication of the catalytic cracking activity of the product as compared with a standard catalyst. It

is based on the relative rate constant (rate of normal hexane conversion per weight of catalyst per unit of time). The standard catalyst is an amorphous silica-alumina cracking catalyst, which is accorded an Alpha value of 1 (rate constant 0.016 sec⁻¹). The Alpha test is described in US 3,354,078, in the Journal of Catalysis, Vol. 4, p. 527
5 (1965), Journal of Catalysis, Vol. 6, p 278 (1966), and Journal of Catalysis, Vol. 61, p 395 (1980). The test was carried out at a temperature of 538°C and at a variable flow rate as described in Journal of Catalysis Vol. 61, p 395 (1980).

Product 2A was calcined at 540°C for 1 hour in nitrogen, and subsequently for 6 hours
10 in air. The calcined product was subjected to an ammonium exchange with a 1 N NH₄Cl solution. The exchanged product was pressed to tablets. The tablets were crushed, and the crushed product was sieved to isolate the fraction with a particle size of 0.4-0.6 mm. These particles were calcined for 6 hours at 550°C. This product had an Alpha value of 2.49, proving enhanced catalytic activity as compared with a
15 standard catalyst.

Example 3

To 106.62 g of demineralised water in a 250 ml PTFE reaction vessel were added
20 successively, with stirring:

- 1.61 g of 99.7 wt.% NaOH,

- 9.68 g of 96 wt.% amphipolar compound

$[\text{C}_6\text{H}_{13}(\text{CH}_3)_2\text{N}^+ - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{N}^+(\text{CH}_3)_2\text{C}_6\text{H}_{13}]\text{Br}_2$,

- 11.49 g of amorphous silica KETJENSIL SM 830; 92.8 wt.% SiO₂, 0.33 wt.% Al₂O₃.

25 The SiO₂:Al₂O₃:H₂O molar ratio in the reaction mixture was 1: 0.002: 34.20.

The mixture was homogenised by stirring for one hour at room temperature. Next, the resulting homogeneous mixture was reacted, with stirring, for 24 hours at a
30 temperature of 95°C, after which the product was filtered off, washed with water, and dried at room temperature.

To determine the characteristics of the product, a small portion was calcined at 540°C and the nitrogen adsorption curve of the calcined product determined.

The process specified above was repeated with a different amount of amphipolar compound. The data obtained in this manner is listed below.

5

No	Molar ratio		SPESA	PV<10nm	MoPD	PV ± 0.1MoPd	
	QUAT	NaOH	m ² /g	ml/g	nm	%	ml/g
3A	0.115	0.230	632	0.292	1.52	38	0.110
3B	0.058	0.230	560	0.290	1.52	29	0.085

Example 4

To 104.51 g of demineralised water in a 250 ml PTFE reaction vessel were added successively, with stirring:

- 1.61 g of 99.7 wt.% NaOH,
- 9.68 g of 96 wt.% amphipolar compound
 $[\text{C}_6\text{H}_{13}(\text{CH}_3)_2\text{N}^+ - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{N}^+(\text{CH}_3)_2\text{C}_6\text{H}_{13}]\text{Br}_2$,
- 2.75 g of aluminium chlorohydrate, 23.5 wt.% Al_2O_3 ,
- 11.49 g of amorphous silica KETJENSIL SM 830, 92.8 wt.% SiO_2 , 0.33 wt.% of Al_2O_3 .

The mixture was homogenised by stirring for one hour at room temperature. Next, the resulting homogeneous mixture was reacted, with stirring, for 24 hours at a temperature of 95°C, after which the product was filtered off, washed with water, and dried at room temperature. The process described above was repeated, except that the quantity of amphipolar compound was varied.

To determine the products' characteristics, small portions of product were calcined at 540°C and their nitrogen adsorption curves determined. The data obtained in this manner is listed below.

No	Molar ratio mol H ₂ O = 34.20				SPESA	PV<10nm	MoPD	PV ± 0.1MoPd	
	QUAT	NaOH	Al ₂ O ₃	SiO ₂	m ² /g	ml/g	nm	%	ml/g
4A	0.115	0.230	0.038	1.00	502	0.255	1.38	24	0.062
4B	0.058	0.230	0.038	1.00	487	0.233	1.42	27	0.064

The Alpha value for product 4A was determined in the manner described in Example 2. The product was found to have an Alpha value of 2.73.

Example 5

To 104.73 g of demineralised water in a 250 ml PTFE reaction vessel were added successively, with stirring:

- 1.61 g of 99.7 wt.% NaOH,
- 4.84 g of 96 wt.% amphipolar compound
[C₆H₁₃(CH₃)₂N⁺ - CH₂-CH₂-CH₂- N⁺(CH₃)₂C₆H₁₃]Br₂,
- 2.75 g of aluminium chlorohydrol, 23.5 wt.% Al₂O₃,
- 11.27 g of amorphous silica KETJENSIL SM 830, 92.8 wt.% SiO₂, 0.33 wt.% Al₂O₃

The molar composition of the mixture QUAT:NaOH:Al₂O₃:SiO₂:H₂O was 0.058:0.230:0.038:1.00:34.20.

The mixture was homogenised by stirring for one hour at room temperature. Next, the resulting homogeneous mixture was reacted, with stirring, for varying periods at different temperatures, after which the product was filtered off, washed with water, and dried at room temperature.

To determine the products' characteristics, small portions of products were calcined at 540°C and their nitrogen adsorption curves determined. The data obtained in this manner is listed below.

No.	Reaction		SPESA	PV<10nm	MoPD	PV ± 0.1 MoPD	
	time Hr	temp °C	m ² /g	ml/g	nm	%	ml/g
5A	24	50	423	0.232	1.27	9	0.020
5B	48	50	442	0.226	1.27	12	0.028
5C	24	95	487	0.233	1.42	27	0.064
5D	48	95	467	0.239	1.33	21	0.050
5E	24	115	347	0.180	1.33	18	0.032

Comparative Example 6

- 5 For reasons of comparison a silicate was prepared in the presence of the amphipolar compound $C_6H_{13}(CH_3)_3N^+Cl^-$.

To 106.62 g of demineralised water in a 250 ml PTFE reaction vessel were added successively, with stirring:

- 10 - 1.61 g of 99.7 wt.% NaOH,
 - 4.52 g of 99.9 wt.% amphipolar compound $C_6H_{13}(CH_3)_3N^+Cl^-$.
 - 11.49 g of amorphous silica KETJENSIL SM 830, 92.8 wt.% SiO_2 , 0.33 wt.% Al_2O_3
- The molar composition of the mixture QUAT:NaOH: Al_2O_3 : SiO_2 : H_2O was 0.115:0.230:0.002:1.00:34.20.

15

The mixture was homogenised by stirring for one hour at room temperature. Next, the resulting homogeneous mixture was reacted, with stirring, for 24 hours at a temperature of 95°C, after which the product was filtered off, washed with water, and dried at room temperature.

- 20 To determine the product's characteristics, a small portion was calcined at 540°C and its nitrogen adsorption curve determined. The data obtained in this manner is listed below.

SPESA	PV<10 nm	MoPD	PV± 0.1 MoPD	
m ² /g	ml/g	nm	%	ml/g
160	0.038	1.63	19	0.007

A comparison of the properties of the product obtained here with those of the silicate prepared in Example 3B, which was prepared in the same manner with the same weight amount of template, shows that the product obtained here has a lower surface area, a lower pore volume in pores with a diameter below 10 nm, and a lower percentage of pores within PV± 0.1 MoPD than the product of Example 3B.

Comparative Example 7

For reasons of comparison an aluminosilicate was prepared in the presence of the amphipolar compound $C_6H_{13}(CH_3)_3N^+Cl^-$.

To 104.51 g of demineralised water in a 250 ml PTFE reaction vessel were added successively, with stirring:

- 1.61 g of 99.7 wt. % NaOH,
- 4.52 g of 99.9 wt. % amphipolar compound $C_6H_{13}(CH_3)_3N^+Cl^-$,
- 2.75 grams of aluminium chlorohydrate, 23.5 wt. % Al_2O_3 ,
- 11.49 g of amorphous silica KETJENSIL SM 830, 92.8 wt. % SiO_2 , 0.33 wt. % Al_2O_3

The molar composition of the mixture QUAT:NaOH: Al_2O_3 : SiO_2 :H₂O was 0.115:0.230:0.038:1.00:34.20.

The mixture was homogenised by stirring for one hour at room temperature. Next, the resulting homogeneous mixture was reacted, with stirring, for 24 hours at a temperature of 95°C, after which the product was filtered off, washed with water, and dried at room temperature.

To determine the product's characteristics, a small portion was calcined at 540°C for 10 hours in air and its nitrogen adsorption curve determined. The data obtained in this manner is listed below.

SPESA	PV<10 nm	MoPD	PV± 0.1 MoPD	
m ² /g	ml/g	nm	%	ml/g
271	0.123	1.27	9	0.011

A comparison of the properties of the product obtained here with those of the aluminosilicate prepared in Example 4B, which was prepared in the same manner with the same weight amount of template, shows that the product obtained here has a lower surface area, a lower pore volume in pores with a diameter below 10 nm, and a lower percentage of pores within PV± 0.1 MoPD.

Example 8

To 104.71 g of demineralised water in a 250 ml PTFE reaction vessel were added successively, with stirring:

- 1.61 g of 99.7 wt.% NaOH,

- 5.89 g of 99.8 wt.% amphipolar compound

$[\text{C}_6\text{H}_{13}(\text{CH}_3)_2\text{N}^+ - \text{CH}_2 - \text{C}(\text{CH}_3)_2 - \text{CH}_2 - \text{N}^+(\text{CH}_3)_2\text{C}_6\text{H}_{13}]_2$,

- 2.75 g of aluminium chlorohydrol, 23.5 wt.% Al_2O_3 ,

- 11.29 g of amorphous silica KETJENSIL SM 830, 92.8 wt.% SiO_2 , 0.33 wt.% Al_2O_3 .

The molar composition of the mixture

QUAT:NaOH: Al_2O_3 : SiO_2 : H_2O was 0.058:0.230:0.038:1.00:34.20.

The mixture was homogenised by stirring for one hour at room temperature. Next, the resulting homogeneous mixture was reacted, with stirring, for 24 hours at a temperature of 95°C, after which the product was filtered off, washed with water, and dried at room temperature.

To determine the product's characteristics, a small portion was calcined at 540°C and the nitrogen adsorption curve of the calcined product determined. The data obtained in this manner is listed below.

SPESA	PV<10 nm	MoPD	PV± 0.1 MoPD	
m ² /g	ml/g	nm	%	ml/g
315	0.171	1.42	21	0.035

Example 9

The amphipolar compound may also be composed of a polymer comprising at least one hydrophilic head group and a hydrophobic part. This is illustrated by the use as template of the linear polymeric compound poly-4-vinyl-1-methyl pyridinium chloride $[(C_7H_7N)CH_3Cl]_x$, MW = 2000.

To approximately 100 g of demineralised water in a 250 ml PTFE reaction vessel were added successively, with stirring:

- 1.61 g of 99.7 wt.% NaOH,
- 2.15 g of poly-4-vinyl-1-methyl pyridinium chloride, 50% in water
- 2.75 grams of aluminium chlorohydrol, 23.5 wt.% Al_2O_3 ,
- 11.49 g of amorphous silica KETJENSIL SM 830, 92.8 wt.% SiO_2 , 0.33 wt.% Al_2O_3 .

The molar composition of the $NaOH:Al_2O_3:SiO_2:H_2O$ mixture was 0.230:0.038:1.00:34.20.

The mixture was homogenised by stirring for one hour at room temperature. Next, the resulting homogeneous mixture was reacted, with stirring, for 24 hours at a temperature of 95°C, after which the product was filtered off, washed with water, and dried at room temperature. The process was repeated using 5.38 and 10.75 g of poly-4-vinyl-1-methyl pyridinium chloride, 50% in water, respectively.

To determine the product's characteristics, a small portion was calcined at 540°C for 10 hours in air and its nitrogen adsorption curve determined. The data obtained in this manner is listed below.

Example	% compound on water base	SPESA	PV<10 nm	MoPD	PV± 0.1 MoPD	
		m ² /g	ml/g	nm	%	ml/g
9A	1.0	251	0.132	1.27	7	0.009
9B	2.5	382	0.216	1.27	9	0.019
9C	5	377	0.202	1.27	9	0.019

The Alpha value for product 9C was determined in the manner described in Example 2. The product was found to have an Alpha value of 2.11.

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Example 10

Example 9C was repeated, except that linear poly-4-vinyl-1-methyl pyridinium chloride was used with a molecular weight of 10,000. The results are given below.

10

SPESA	PV<10 nm	MoPD	PV± 0.1 MoPD	
m ² /g	ml/g	nm	%	ml/g
413	0.237	1.27	9	0.021

Comparative Example 11

An aluminosilicate was prepared in the presence of linear poly-4-vinylpyridine, MW = 2000.

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To 96.66 g of demineralised water in a 250 ml PTFE reaction vessel were added successively, with stirring:

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- 1.61 g of 99.7 wt.% NaOH,
- 13.45 g poly-4-vinylpyridine, 40% in water
- 2.75 grams of aluminium chlorohydrate, 23.5 wt.% Al₂O₃,
- 11.49 g of amorphous silica KETJENSIL SM 830, 92.8 wt.% SiO₂, 0.33 wt.% Al₂O₃.

The gel contained 5.0 wt.% of poly-4-vinylpyridine, calculated on the amount of water. The molar composition of the mixture $\text{NaOH}:\text{Al}_2\text{O}_3:\text{SiO}_2:\text{H}_2\text{O}$ was 0.230:0.038:1.00:34.20.

The mixture was homogenised by stirring for one hour at room temperature. Next, the resulting homogeneous mixture was reacted, with stirring, for 24 hours at a temperature of 95°C, after which the product was filtered off, washed with water, and dried at room temperature.

To determine the product's characteristics, a small portion was calcined at 540°C for 10 hours in air and its nitrogen adsorption curve determined. The data is listed below.

SPESA	PV<10 nm	MoPD	PV± 0.1 MoPD	
m ² /g	ml/g	nm	%	ml/g
158	0.054	1.27	11	0.006

A comparison of this data with the data obtained in Example 9C shows that the product obtained here has a lower surface area and a lower pore volume in pores with a diameter below 10 nm than the product of Example 9C. This shows that the use of a template with cationic head groups leads to a better product than the use of a template with neutral head groups.

CLAIMS

1. A process for synthesising a porous inorganic material having an MoPD of 0.8-2.0 nm, characterised in that the synthesis is performed in the presence of templates containing one or more amphipolar compounds having at least two cationic or anionic head groups and a hydrophobic part.

2. A process according to claim 1, characterised in that at least a portion of the head groups of the amphipolar compound has a cationic nature.

3. A process according to claim 2, characterised in that the amphipolar compound satisfies formula (1)



wherein

Q, Q', and Q'' may be the same or different and represent a nitrogen atom or phosphorus atom,

n and m each independently have a value of 1-8,

y has a value of 0-1000,

R₁, R₁', and R₁'' are independently selected from optionally substituted alkyl groups having 3-12 carbon atoms and optionally substituted aryl groups having 4-12 carbon atoms, R₂, R₂', R₂'', R₃, R₃', and R₃'' are each independently selected from hydrogen and optionally substituted alkyl groups having 1-6 carbon atoms, with the proviso that each of R₁, R₁', and R₁'' contains more carbon atoms than each of R₂ and R₃, R₂' and R₂'' and R₃'', respectively, R₄, R₄', R₅, and R₅' may be the same or different and are selected from hydrogen and optionally substituted methyl and ethyl, with the proviso that if n, m, and/or y has a value higher than 1, the additional groups R₄, R₅, R₄', R₅', R₁', and R₂' formed as a result need not necessarily have the same value as the other groups thus designated.

4. A process according to claim 3, characterised in that in formula (1) R4, R4', R5, and R5' all are either hydrogen or methyl.
5. A process according to claim 3 or 4, characterised in that in formula (1) R1, R1', and R1" all have 4-10 carbon atoms, and R2, R2', R2", R3, R3', and R3" are all selected independently from methyl, ethyl, and propyl.
6. A process according to claim 3, 4, or 5, characterised in that in formula (1) n and m have a value of 2-4, and y is 0-10.
7. A process according to claim 1 or 2, characterised in that the template is made up of polymers which comprise at least two cationic or anionic head groups and a hydrophobic part.
8. A process according to claim 7, characterised in that the polymer is a poly-4-vinyl pyridinium derivative.
9. A porous mixed metal oxide which contains at least 0.2 wt.% of a first oxide, and a total of further oxides of at most 99.8 wt.% having an MoPD of 0.8-2.0 nm.
10. A porous mixed metal oxide according to claim 9, characterised in that it is a metallosilicate.
11. A porous mixed metal oxide according to claim 10, characterised in that it is an aluminosilicate.
12. Use of the porous mixed oxide according to any one of claims 9, 10, and 11 in catalysis.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 96/04781

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B37/00 C01B39/06 C01B39/04 B01J29/00 B01J29/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
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INTERNATIONAL SEARCH REPORT

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